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HEAT-RESISTANT RESIN COMPOSITION
[Tainetsusei Jushi Soseibutsu]

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Specification

1. Title of the invention

A heat-resistant resin composition

2. Patent Claims

1. A heat-resistant resin composition inclusive of a titanium chelate and a polyester resin in possession, in the molecule chain thereof, of an amide-imide bond.

2. A heat-resistant resin composition specified in Claim 1 wherein said polyester resin in possession, in the molecule chain thereof, of an amide-imide bond is a resin obtained by using an amide-imide oligomer obtained by reacting an isocyanate compound, a tribasic acid anhydride, and a lactam.

3. A heat-resistant resin composition specified in Claim 1 or 2 wherein said polyester resin in possession, in the molecule chain thereof, of an amide-imide bond is a resin obtained by using, with respect to said polyester resin in possession, in the molecule chain thereof, of an amide-imide bond, 20 ~ 80 wt% of said amide-imide oligomer.

3. Detailed explanation of the invention

It has become mandatory, for purposes of reducing the sizes & weights of electric appliances and of improving the reliabilities of the same, to further improve the heat resistance, abrasion resistance, thermal impact resistance, hydrolyzability, etc. of enamel wires. The present inventors obtained a polyamide-imide ester varnish capable of satisfying the above-mentioned requirements by modifying a polyester varnish with a polyamide-imide resin. Such practical performances as high-speed bakability, cut-through potential, etc. of this type of varnish become improved in a case where it is used together, as a curing agent, with a tetraalkyl titanate, as in the

¹ Numbers in the margin indicate pagination in the foreign text.

cases of ordinary polyester varnishes. Generally speaking, in a case where a tetraalkyl titanate is added, as a curing agent, to an enamel wire varnish, the former is normally added dropwise, for the purpose of preventing the varnish viscosity gain as a result of addition, within a temperature range of 100 ~ 150°C over a period of approximately 0.5 ~ 3 hours. It was discovered that, although an ordinary polyester varnish to which the tetraalkyl titanate has been thus added is unaccompanied by such phenomena as the resin phase separation & film transparency loss, a film transparency loss is occasionally incurred in a case where a tetraalkyl titanate is added to the above-mentioned polyamide-imide ester varnish under the aforementioned conditions. /2

The present inventors compiled intensive researches for the purpose of avoiding this transparency loss phenomenon, as a result of which the present invention has been completed after it had been discovered that the film transparency loss phenomenon can be prevented by adding, instead of the tetraalkyl titanate, a titanium chelate to an amide-imide ester varnish.

The present invention concerns a heat-resistant resin composition inclusive of a titanium chelate and a polyester resin in possession, in the molecule chain thereof, of an amide-imide bond.

The polyester resin of the present invention in possession, in the molecule chain thereof, of an amide-imide bond can be obtained by (1) initially synthesizing an amide-imide oligomer and by (2) then thermally reacting the same with a polyester resin or by thermally reacting the same with an alcohol component & an acid component.

The amide-imide oligomer is obtained by reacting an isocyanate compound and a tribasic acid anhydride within a polar solvent such as cresol, phenol, N-methylpyrrolidone, etc. Phenolic solvents, above all cresol, are desirable as synthesizing solvents in consideration of costs. In a case where a lactam is additionally used as a reactive component, the turbidity of a varnish is unlikely to occur even in a case where the molecular weight of the amide-imide oligomer becomes higher, and therefore, the use of the lactam is preferred.

Favorable isocyanate compounds are instantiated by aromatic diisocyanates such as toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, etc. In a case where an isocyanurate

ring-containing polyisocyanate is used partially as said isocyanate compound, the turbidity of the varnish is unlikely to occur. Usable isocyanurate ring-containing polyisocyanates are instantiated by isocyanurate ring-containing polyisocyanates obtained as a result of the trimerizing reactions of such diisocyanates as toluylene diisocyanate, 4,4'-diphenylmethane diisocyanate, isophorone diisocyanate, etc.

Tribasic acid anhydrides are instantiated by trimellitic anhydride, butanetricarboxylic anhydride, etc.

The use of ϵ -caprolactam as the lactam is desirable in consideration of the reactivity & cost. It is desirable, in consideration of the heat resistance, for the utilization ratio of the lactam to be less than 100 eq% of the total isocyanate equivalent. In the above, 1 mole of lactam is construed as 2 equivalents.

It is desirable, in consideration of the heat resistance & plasticity, for the utilization ratios of the isocyanate compound & tribasic acid anhydride to be confined to a range of 0.6 ~ 1.5, preferably 0.7 ~ 1.15, in terms of the equivalent ratio of isocyanato groups with respect to carboxyl groups and.

All the reaction feed materials may be simultaneously fed, although they may be fed stepwise depending on sought objectives. As far as the reaction temperature is concerned, it is desirable for a main reaction to be induced, upon the feeding of all components, within a range of 195 ~ 220°C.

There are no special restrictions on polyester resins to be thermally reacted with the amide-imide oligomer used in the present invention. It is desirable to use, as acid components selected for manufacturing said polyester resins, terephthalic acid, isophthalic acid, and their derivatives such as dimethyl terephthalate, dimethyl isophthalate, etc. Divalent or higher alcohols are normally used as alcohol components. Usable divalent alcohols may, for example, be instantiated by ethylene glycol, neopentyl glycol, 1,4-butanediol, 1,6-hexanediol, 1,6-cyclohexanedimethanol, etc., whereas usable trivalent or higher alcohols may, for example, be instantiated by glycerin, trimethylolpropane, tris-2-hydroxyethyl isocyanurate, pentaerythritol, etc. It is desirable, in consideration of the heat

resistance & abrasion resistance, for at least 30 eq% of the entire alcohol component to be accounted for by trivalent or higher alcohols. It is especially desirable to use glycerin in consideration of the crazing resistance and tris-2-hydroxyethyl isocyanurate in consideration of the heat resistance & refrigerant resistance.

As far as the equivalent ratio between the acid & alcohol is concerned, it is desirable to use an excess of the alcohol at an alcohol excess ratio of 1% ~ 60%. There are no special restrictions on methods for synthesizing polyester resins.

As far as the present invention is concerned, there are no special restrictions on the alcohol components & acid components to be thermally reacted with the amide-imide oligomer, although 3 it is desirable to use the acid components & alcohol components instantiated with regard to the above-mentioned polyester resins. As far as the equivalent ratio between the acid & alcohol is concerned, it is desirable to use an excess of the alcohol at an alcohol excess ratio of 1% ~ 60%.

It is desirable, in consideration of the heat resistance & varnish stability, for the utilization ratio of the amide-imide oligomer with respect to the polyester resin in possession, in the molecule chain thereof, of an amide-imide bond to be confined to a range of 20 ~ 80 wt%. There are no special restrictions on conditions for thermally reacting the amide-imide oligomer with the polyester resin or the acid component & alcohol component so long as an esterifying reaction, transesterifying reaction, amidoesterifying reaction, etc. can substantially be induced. The reaction is normally induced within a temperature range of 120 ~ 240°C in the presence of a trace of an esterification catalyst (e.g., tetrabutyl titanate, lead acetate, dibutyltin dilaurate, etc.). It goes without saying that an additional solvent (e.g., cresol, etc.) can be supplemented in the course of synthesis in accordance with the viscosity.

The titanium chelate used in the present invention is an extant publicly known compound and can be synthesized by various methods, and one known example is obtained by thermally reacting, as a ligand precursor, a chelating agent with a tetraalkyl titanate {F. Schmidt, *Angew. Chem.*, 64, 536 (1952)}. Such tetraalkyl titanates may, for example, be instantiated by tetrabutyl

titanate, tetraisopropyl titanate, etc. The titanium chelate is added to a solution inclusive of the polyester resin in possession, in the molecule chain thereof, of an amide-imide bond, whereas it is usually desirable for the addition temperature to be equal to or higher than normal temperature and 100°C or lower, and a temperature range of 50 ~ 80°C is especially desirable. In a case where the temperature is excessively high, it is undesirable in that the ligand becomes dissociated and that the enamel wire film transparency loss preventive effect becomes adversely affected. It is desirable for the utilization ratio of the titanium chelate with respect to 100 parts by weight of the resin to be confined to a range of 1 ~ 10 parts by weight. Usable chelate compounds are instantiated by glycols such as octylene glycol, hexanediol, etc.; β -diketones such as acetylacetone, etc.; hydroxycarboxylic acids such as lactic acid, salicylic acid, etc.; keto esters such as ethyl acetoacetate, etc.; keto alcohols such as diacetone alcohol, etc.; etc.

Either the heat-resistant resin composition of the present invention as it is or, if necessary, a mixture obtained by adding, to the same, 0.1 ~ 25 wt% (with respect to the resin content) of an additive(s) such as an epoxy resin, phenol-formaldehyde resin, polyisocyanate generator, organic acid metal salt, polyether resin, polyamide resin, polyester-imide resin, polyhydantoin resin, alkoxy-modified amino resin, polysulfone resin, furan resin, phenoxy resin, etc. is coated, either directly or together with another insulating coating film, on an electric conductor, as a result of which an insulated electric cable becomes obtained. There are no special restrictions on conditions for manufacturing the insulated electric cable, and routinely designated conditions suffice.

The heat-resistant resin composition thus obtained can also be used as a heat-resistant coating material.

The present invention will be explained with reference to application examples & comparative examples.

Comparative Example 1

Component	Gram(s)	Mole(s)
Dimethyl terephthalate	518.0	2.67
Diethylene glycol	113.0	1.83
Glycerin	92.0	1.0
Tetrabutyl titanate (catalyst)	0.72	
Cresol	38.0	

After the aforementioned components had been charged into a four-neck flask equipped with a thermometer, an agitation mechanism, & a fractionalizing tube, the temperature was elevated to 150°C within a nitrogen stream, and after the reaction temperature had been elevated to 230°C over a 6-hour period in a state where the methanol distilled as a result of the reaction was being removed, the reaction was continued at the same temperature till the gelation time on a 250°C hot plate had become 160 sec. or less.

Comparative Example 2: Synthesis of isocyanurate ring-containing polyisocyanate

Component	Gram(s)
Toluylene diisocyanate	600
Xylene	600
2-dimethylaminoethanol (catalyst)	1.8

After the aforementioned components had been charged into a four-neck flask equipped /4 with a thermometer & an agitation mechanism, the temperature was elevated to 140°C within a nitrogen stream, and the reaction was continued at the same temperature till the internalization ratio of isocyanato groups (initial concentration: 48 wt%) had reached 25 wt%.

According to the infrared spectrum of the obtained product, absorptions of isocyanurate rings were acknowledged at $1,710\text{ cm}^{-1}$ & $1,410\text{ cm}^{-1}$, whereas the absorption of isocyanato groups was acknowledged at $2,260\text{ cm}^{-1}$.

Comparative Example 3

(1): Synthesis of polyamide-imide resin

Component	Gram(s)	Equivalent(s)
4,4'-diphenylmethane diisocyanate	117.5	0.94
Isocyanurate ring-containing polyisocyanate synthesized in Comparative Example 2	26.7	0.08
ϵ -caprolactam	36.7	0.65
Trimellitic anhydride	96.0	1.00
Cresol	180.0	
Xylene	10.0	

After the aforementioned components other than the trimellitic anhydride had been charged into a four-neck flask equipped with a thermometer, an agitation mechanism, & a fractionalizing tube, the temperature was elevated to 170°C within a nitrogen stream, and the contents were then

reacted over a 60-min. period. After the trimellitic anhydride had subsequently been added, the temperature was elevated to 210 ~ 215°C, and the reaction was continued until the Gardner second count of a cresol solution with a resin content of 25 wt% at 25°C had reached 160 sec. The methanol-insoluble content $\eta_{sp/c}$ (DMF, 0.5%) of the obtained polyamide-imide was 0.26.

Comparative Example 4

After 400 g of the resin solution obtained in Comparative Example 3 had been added to 500 g of the resin solution obtained in Comparative Example 1, the temperature was elevated to 170°C, and after 7 g of tetrabutyl titanate had subsequently been added, the temperature was maintained at 170°C over a 6-hour period. Next, the obtained product was diluted with a cresol/xylene = 7/3 (weight ratio) solution until the Gardner second count thereof at 25°C had reached 80 sec. As a result, a solution with a non-volatile content of 41 wt% and a viscosity (at 30°C) of 60 P was obtained.

600 g of this solution was sampled, and 8 g of zinc octenate & 24 g of tetrabutyl titanate (as a 50 wt% cresol solution) were added dropwise to this solution at a temperature of 80°C over a 90-min. period. As a result, the solution was converted into a semi-gel, and it was impossible to obtain a varnish capable of tolerating evaluations.

Comparative Example 5

600 g of the solution with a non-volatile content of 41 wt% obtained in Comparative Example 4 was sampled, and 8 g of zinc naphthenate and 24 g of tetrabutyl titanate (as a 50 wt% cresol solution) were added dropwise to this solution at a temperature of 130°C over a 90-min. period.

Application Example 1

600 g of the solution with a non-volatile content of 41 wt% obtained in Comparative Example 4 was sampled, and 8 g of zinc naphthenate and 15 g of a titanium chelate solution inclusive, as a chelating agent, of acetylacetone (non-volatile content: 70 wt%; TAA, manufactured by Matsumoto Pharmaceutical K.K.) were added dropwise to this solution at a temperature of 80°C over a 90-min. period.

Application Example 2

(1): Synthesis of amide-imide oligomer

Component	Gram(s)	Equivalent(s)
Isocyanurate ring-containing polyisocyanate synthesized in Comparative Example 2 (50 wt% solution)	50.0	0.15
4,4'-diphenylmethane diisocyanate	113.3	0.91
Trimellitic anhydride	109.4	1.14
Cresol	260.0	
ϵ -caprolactam	31.1	0.55

After the aforementioned components other than the trimellitic anhydride had been charged into a four-neck flask equipped with a thermometer, an agitation mechanism, & a fractionalizing tube, the contents were reacted at 160°C over a 1-hour period, and after the trimellitic anhydride had subsequently been added, the temperature was elevated to 205 ~ 210°C, and the reaction was continued until the Gardner second count of a 20 wt% cresol solution at 25°C had reached 25 sec.

(2): Synthesis of a polyester resin in possession, in the molecule chain thereof, of an amide-imide bond

Component	Gram(s)	Equivalent(s)
Dimethyl terephthalate	232.8	2.4
Tris-2-hydroxyethyl isocyanurate	250.6	2.88
Tetrabutyl titanate	0.5	

After the aforementioned components had been further added to the obtained product, the temperature was elevated to 190°C, and the reaction was continued at the same temperature till the gelation time on a 250°C gel disc (resin: 0.2 g) had reached 200 sec. Next, the obtained product /5 was diluted with a cresol/xylene = 7/3 (weight ratio) solution until the Gardner second count thereof at 25°C had reached 75 sec. Next, 32 g of a titanium chelate solution inclusive, as a chelating agent, of acetylacetone (non-volatile content: 70 wt%; TAA, manufactured by Matsumoto Pharmaceutical K.K.) & 20 g of zinc naphthenate were added dropwise to this solution at a temperature of 70°C over a 90-min. period. The non-volatile content of the obtained varnish (200°C, 2 hrs) was 38 wt%, whereas its viscosity at 30°C was 45 P.

An enamel wire was obtained by bake-coating the varnish obtained in Comparative Example 3, Application Example 1, or Application Example 2 onto a copper wire with a diameter of 1 mm. The results are shown in Table I. As control data, the enamel wire performances of standard polyester varnish WH-407 (manufactured by Hitachi Kasei K.K.) are also shown. The enamel wire performances were measured in compliance with JIS C 3003.

Table I: Enamel wire performances

	Comparative Example 3	Application Example 1	Application Example 2	WH-407
Physical appearance	Many fine particles, transparent, & absence of luster	Favorable	Favorable	Favorable
Plasticity in terms of autonomous wire coatability	Favorable	Favorable	Favorable	Favorable
Heat-resistant impact profile in terms of autonomous wire coatability pass temperature (°C, 1 hr)	200	200	200	130
Thermal softening point (load: 700 g, °C)	310	312	385	300

As the results of Comparative Example 3, Comparative Example 4, Application Example 1, Application Example 2, and Table I indicate, in a case where a tetraalkyl titanate is added to a polyester resin in possession, in the molecule chain thereof, of an amide-imide bond, a semi-gelled varnish becomes obtained at 80°C, due to which it becomes impossible to obtain a usable varnish, whereas in a case where the same is added at a higher temperature for the purpose of inhibiting the

varnish viscosity gain, the physical appearance of the enamel wire may deteriorate due to the generation of fine particles, transparency, & lack of luster. In a case where a titanium chelate is used, in contrast, no varnish viscosity gain is incurred even at a low addition temperature, and the enamel wire obtained by bake-coating the obtained varnish is excellent in terms of both physical appearances & performances. Thus, the heat-resistant resin composition obtained by combining a titanium chelate with a polyester resin in possession, in the molecule chain thereof, of an amide-imide bond is useful from an industrial standpoint in that it yields enamel wires bearing favorable physical appearances & performances.

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